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## COMPLETE SPECIFICATION

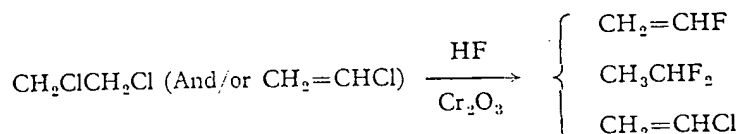
### Improvements in and relating to Fluorination

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America (assignee of JOSEPH PETER HENRY, CHARLES EDWARD RECTENWALD and JARED WILSON CLARK), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing vinyl fluoride and difluoroethane by the fluorination of ethylene dichloride and vinyl chloride. 15

This invention comprises a process of heating a mixture comprising ethylene dichloride, or vinyl chloride, or both, and hydrogen fluoride at a temperature between 200° C. and 500° C. in the presence of chromium oxide catalyst. The product mixture comprises vinyl fluoride and 1,1-difluoroethane. 20

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25 The process can be conducted either batchwise or continuously. In a preferred method, the reaction mixture is passed as vapor continuously over chromium oxide catalyst contained in a stainless steel tube or nickel-pipe reactor. The effluent product gas is processed through a water scrubber and a drying unit, and then the product mixture is condensed and recovered. The components of the product mixture are conveniently separated by distillation. 30

35 The process temperature can vary between 200° C. and 500° C. with the preferred temperature range being between 300° C. and 400° C. The higher the temperature in the range between 300° C. to 400° C., the higher the yield of unsaturated compounds in the product. For example, at a given conversion, an increase of 50° C. in the reaction temperature more than doubles the ratio of vinyl fluoride to 1,1-difluoroethane in the product. 40

45 The process can be performed at atmospheric pressure, or at subatmospheric and superatmospheric pressures. The use of pressures higher than atmospheric pressure increases the yield of saturated products and facilitates the recovery of the low boiling products and the hydrogen chloride by-product. 50

Pressures of 20 atmospheres have been advantageously employed. The use of pressure is desirable if an increased quantity of 1,1-difluoroethane is sought. 55

The residence time of the feed mixture in the reactor varies widely depending on the reaction temperature employed and the particular proportion of compounds desired in the recovered product mixture. The residence time will range from as little as one second at the higher temperature to over several minutes at the lower temperatures. In a typical reaction sequence, the residence time of the vapor in the reactor will vary between one second and ten seconds at reaction temperatures between 200° C. and 500° C. A residence time between two and five seconds at a temperature between 300° C. and 400° C. is particularly preferred. At shorter residence times, a superior yield of fluorinated products is obtained with vinyl chloride as the starting material as compared to ethylene dichloride. 60

The molar ratio of hydrogen fluoride to halo-hydrocarbon material (e.g., vinyl chloride and ethylene dichloride) in the feed mixture can vary in the range between 2 and 75

[Price 4s. 6d.]



20 moles of hydrogen fluoride for each mole of halo-hydro-carbon feed, with the preferred molar ratio being between 3 and 10 moles of hydrogen fluoride per mole of halo-hydro-carbon feed. An equivalent conversion of vinyl chloride feed can be obtained with about half as much hydrogen fluoride as is required for ethylene dichloride. For example, a feed ratio of 5 moles of hydrogen fluoride per mole of vinyl chloride results in about the same conversion per pass as can be obtained with 10 moles of hydrogen fluoride per mole of ethylene dichloride.

The fluorination of ethylene dichloride under the conditions specified herein produces a product mixture which comprises vinyl fluoride, vinyl chloride and 1,1-difluoroethane. The particular proportions of components produced in the product mixture vary with the process conditions employed in a given reaction sequence. By manipulation of reaction conditions and the composition of the feed mixture, the production of one component of the product mixture can be enhanced concurrently with the suppression of the formation of the other components.

Vinyl fluoride can be obtained as the sole product of the present process by heating a mixture comprising ethylene dichloride and hydrogen fluoride in a molar ratio between 2 and 20 moles of hydrogen fluoride per mole of ethylene dichloride at a temperature between 250° C. and 400° C. in the presence of a chromium oxide catalyst for a residence time between two and five seconds. The product mixture comprising vinyl fluoride, vinyl chloride and 1,1-difluoroethane is recovered and the vinyl chloride and 1,1-difluoroethane are recycled to the feed mixture at the beginning of the process. Alternatively if 1,1-difluoroethane is desired this compound is recovered and the vinyl chloride and vinyl fluoride recycled. The hydrogen fluoride employed in the feed mixture is adjusted to provide for the consumption of hydrogen fluoride required by the total moles of organic feed.

The chromium oxide catalyst of the process can be employed in several forms. The catalyst can be in the form of granular hydrous chromium oxide which is formed as a precipitate in the reaction of ammonium hydroxide on an aqueous chromium chloride solution. The same hydrous chromium oxide can be employed in the form of cubes prepared from the precipitate when it is in the form of a partially dried paste. In another variation, the hydrous chromium oxide can be mixed with a minor portion of chromium chloride and pelleted. The chromium chloride in the mixture serves as a lubricant to facilitate the pelleting operation. In another variation, chromium chloride and aluminium chloride can be treated with ammonium hydroxide to form a coprecipitate. The resulting coprecipitate can be used in the form of granules,

cubes or pellets as described above. In still another variation, the chromium oxide is employed on an alumina support. Porous alumina is impregnated with an aqueous solution of chromium trioxide. The material is then dried and reduced at elevated temperatures in an atmosphere of hydrogen. The catalyst so produced is particularly suitable in the practice of this invention. The porous alumina employed may be either alpha-alumina and kappa-alumina.

To recover conveniently the product mixture produced by the process, the effluent gas is scrubbed with water, dried with a drying agent, e.g. silica gel, activated alumina or a molecular sieve, and then the product mixture is condensed and recovered. The product mixture is fractionally distilled to separate the mixture into its components, and one or more components can be recycled if desired. This process is easily adapted for commercial operation by the use of suitable refrigeration and compression systems to accomplish the required separation and recycling procedures.

The process of the present invention provides a commercially feasible method of producing vinyl fluoride and 1,1-difluoroethane from ethylene dichloride or vinyl chloride which are readily available starting materials.

The following examples will serve to illustrate specific embodiments of the invention.

#### EXAMPLE 1

This example illustrates the preparation of chromium catalysts useful in the practice of this invention.

(a) Water (1145 milliliters) and ammonium hydroxide solution (588 grams, 28 per cent  $\text{NH}_3$ ) were placed in a flask equipped with a mechanical stirrer and a dropping funnel. A chromic chloride solution (520 grams of a 37 per cent chromic solution and one liter of water) was added dropwise to the contents of the flask with stirring during a one-hour period. The resulting precipitate was separated from the supernatant liquid, and the precipitate was washed with water to remove ammonium chloride. The precipitate was then placed in a shallow pan and dried in a vacuum oven at 70° C. When the material was partially dried, the paste was cut into small squares so that the hydrous chromium oxide catalyst after complete drying was in the form of 6.4 mm cubes. The final drying of the hydrous chromium oxide catalyst was accomplished at a temperature of 480° C. under an atmosphere of nitrogen.

(b) Approximately 600 milliliters (247 grams) of hydrous chromium oxide prepared in the manner of section (a) above was mixed with 45 grams of anhydrous chromic chloride, and the mixture was ground in a ball mill for sixteen hours. The fine powder obtained was pelleted employing 2.4 mm. dies.

(c) Approximately 344 grams (2.5 moles) of aluminium chloride was dissolved in 15

liters of water. This solution was blended with a solution containing 395 grams (2.5 moles) of chromic chloride in 3.67 liters of water. The resulting solution was fed with vigorous agitation into a flask containing 920 grams of 28 per cent ammonium hydroxide diluted with 4 liters of water. The resulting precipitate was separated and washed several times with water. The material was transferred to shallow pans, cut into 6.4 mm. cubes and dried in an oven at 60° C., and then dried in a furnace at 450° C. for two days.

(d) Approximately 67.1 grams of chromium trioxide ( $\text{CrO}_3$ ) was then dissolved in 102 grams of water. This solution was then added slowly with frequent agitation to 300 cubic centimeters of Alcoa (a Registered Trade Mark) F-10 activated alumina (gamma- $\text{Al}_2\text{O}_3$ , particle size from 3.38 to 3.36 mm.) contained in an evacuated flask. The material was partially dried by heating the flask under reduced pressure. It was then transferred to a nickel reactor 2.5 cm. inside diameter and heated to 200° C. under a constant flow of nitrogen to complete the drying of the catalyst. The orange-red catalyst was then reduced with hydrogen for four hours at 250° C. to 300° C. to produce the green-colored chromium oxide ( $\text{Cr}_2\text{O}_3$ ) supported on gamma-alumina.

In a similar manner, a catalyst of chromium oxide supported on alpha-alumina was prepared. The alpha-alumina supported catalyst had the advantage of additional mechanical strength.

#### EXAMPLE 2

A mixture of ethylene dichloride and hydrogen fluoride in a mole ratio of 1 to 4 was passed in vapor phase over a chromium oxide ( $\text{Cr}_2\text{O}_3$ ) on gamma-alumina catalyst (Example

1 d) at a temperature of 350° C. for a contact time of three seconds. The effluent product gas was scrubbed free of hydrogen fluoride and condensed in a dry ice-cooled trap. Approximately 20 per cent of the product was vinyl fluoride and 1,1-difluoroethane, and the remaining product material was vinyl chloride. The recovery of organic material was over 98 per cent.

#### EXAMPLE 3

Vinyl chloride and hydrogen fluoride in a 1 to 2 molar ratio were passed in a vapor state over a chromium oxide on gamma-alumina catalyst (prepared as in Example 1 d) at a temperature of 350° C. for a contact time of three seconds. The effluent product gas was scrubbed to remove excess hydrogen and then condensed. Distillation of the recovered product mixture indicated that 29 per cent conversion of the vinyl chloride had occurred. The composition of the recovered product mixture was 72.2 per cent vinyl chloride, 20 per cent vinyl fluoride and 7.6 per cent 1,1-difluoroethane.

#### EXAMPLE 4

This example illustrates the effect of feed mole ratio in the fluorination of ethylene dichloride.

Two fluorination runs were conducted employing a nickel reactor 2.5 cm. inside diameter containing chromium oxide on gamma-alumina catalyst prepared in the manner of section (d) of Example 1. The reaction conditions and product yields are listed in Table 1.

At the completion of each run, the catalyst was oxidized at the reaction temperature with air, followed by oxygen. The time required for regeneration was about three and one-half hours.

TABLE 1

	A	B
Reaction temperature (°C.)	350	350
Contact time (seconds)	3	3
Mole ratio (HF:ethylene chloride)	4	10
Product Distribution		
Vinyl fluoride	9.1	19.0
Difluoroethane	6.4	11.6
Vinyl chloride	84.5	68.3

## EXAMPLE 5

This example illustrates the effect of temperature and contact time in the fluorination of ethylene chloride.

Employing the nickel reactor and chromium

oxide on alumina catalyst of Example 4, four fluorination runs were conducted. The reaction conditions and product yields are listed in Table 2.

TABLE 2

	C	D	E	F
Reaction temperature (°C.)	350	375	400	400
Contact time (seconds)	3	3	2	5
Mole ratio (HF/ethylene dichloride)	10	10	10	10
Product Distribution				
Vinyl fluoride	19.0	27.1	25.0	30.8
Difluoroethane	11.6	9.1	4.2	5.2
Vinyl chloride	68.3	63.8	68.6	61.1

## EXAMPLE 6

This example illustrates the fluorination of ethylene dichloride with recycle of vinyl chloride.

Three fluorination runs were conducted employing the same nickel reactor and chromium oxide on alumina catalyst as used in

Example 4. Vinyl chloride was recycled to the succeeding run. The reaction conditions and yields are listed in Table 3. Vinyl fluoride amounted to about 70 per cent of the fluorinated product, with the balance being 1,1-difluoroethane.

TABLE 3

(375° C.; 10:1, HF/organic compound; 4 sec. contact time)

Feed Composition (mole per cent)		Product Composition (mole per cent)		
Vinyl Chloride	Ethylene Dichloride	Vinyl Fluoride	Difluoroethane	Vinyl Chloride
60.6	39.4	32.6	10.7	56.7
53.8	46.2	32.1	14.0	53.9
50.4	49.6	33.4	14.8	51.8

As demonstrated by the present specification, in the fluorination process: (1) the ratio of total fluorine-containing products to vinyl chloride can be increased by increasing the mole ratio of hydrogen fluoride to organic feed material and by using longer contact times, (2) the ratio of vinyl fluoride to 1,1-difluoroethane in the product can be raised by increasing the reaction temperature or lowered by employing superatmospheric pressure, (3) ethylene dichloride conversion is sub-

stantially complete, and (4) recycle of vinyl chloride results in a higher conversion to fluorinated product than by once-through operations.

## WHAT WE CLAIM IS:—

1. A process for preparing fluorinated hydrocarbons comprising heating a reactant mixture of ethylene dichloride or vinyl chloride or both and hydrogen fluoride at a temperature between 200° C. and 500° C. in the presence of chromium oxide catalyst.

2. A process as claimed in claim 1 in which the reaction time is between 1 and 10 seconds.
- 5 3. A process as claimed in claim 1 or 2 in which the reaction temperature is between 300° C. and 400° C.
4. A process as claimed in claim 3 in which the reaction time is between 2 and 5 seconds.
- 10 5. A process as claimed in any of the preceding claims in which the reactant mixture is passed as a vapor over the chromium oxide catalyst contained in a stainless steel tube or nickel pipe reactor.
- 15 6. A process as claimed in any of the preceding claims in which the molar ratio of hydrogen fluoride in halocarbon in the reactant mixture is between 2:1 and 20:1.
- 20 7. A process as claimed in claim 6 in which the molar ratio is between 3:1 and 10:1.
8. A process as claimed in any of the preceding claims in which ethylene dichloride is fluorinated and vinyl chloride formed in the reaction is recycled to the reactant mixture. 25
9. A process as claimed in any of the preceding claims in which vinyl chloride and vinyl fluoride are recycled to the reactant mixture and 1,1-difluoroethane is recovered as product. 30
10. A process for preparing fluorinated hydrocarbons substantially as hereinbefore described with reference to and as illustrated in any of Examples 2 to 6. 35
11. Fluorinated hydrocarbons whenever prepared by the process as claimed in any of the preceding claims.

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